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(71)Applicant : SAMSUNG DISPLAY DEVICES
CO LTD

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(72)Inventor : CHO HUN-GOO

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(54) ELECTROLYTE FOR LITHIUM ION BATTERY AND LITHIUM ION BATTERY USING IT

(57)Abstract:

PROBLEM TO BE SOLVED: To form a uniform fine SEI film on the surface of a negative electrode active material so as to suppress the decomposition action of an electrolyte by adding a specific quantity of surfactant to a mixed organic solvent and a Li metallic salt dissolved in the solvent.

SOLUTION: An electrolyte for a Li ion battery consists of mixed organic solvent, Li metallic salt dissolved in this solvent, and a surfactant of 0.01-5% by weight to the total weight of the mixed organic solvent and the Li metallic salt. When an addition amount of the surfactant is less than 0.01% by weight, a SEI film formed on the negative electrode active material remains ununiform. When the addition amount exceeds 5% by weight, the SEI film becomes unnecessarily thick and ion conductivity is lowered. When the SEI film provided with high ion conductivity to Li ions is formed, Li ions are received/released reversibly through the film while reduction of the electrolyte is reduced, so that a reversibility of the battery can be increased.

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CLAIMS

[Claim(s)]

[Claim 1] The electrolytic solution for Li ion cells which contains 0.01 - 5% of the weight of a surfactant on the basis of the total amount of Li metal salt dissolved in the mixed organic solvent and said solvent, and said mixed organic solvent and Li metal salt.

[Claim 2] Said mixed organic solvent is the electrolytic solution for Li ion cells according to claim 1 characterized by including a high dielectric constant solvent and a hypoviscosity solvent.

[Claim 3] The electrolytic solution for Li ion cells according to claim 2 characterized by being chosen from the group which said high dielectric constant solvent becomes from ethylene carbonate, propylene carbonate, and a gamma butyrolactone.

[Claim 4] The electrolytic solution for Li ion cells according to claim 2 characterized by being chosen from the group which said hypoviscosity solvent becomes from dimethyl carbonate, diethyl carbonate, and dimethoxyethane.

[Claim 5] Said Li metal salt is LiPF₆, LiAsF₆, LiCF₃ SO₃, LiN (CF₃ SO₂)₃, and LiBF₆. And LiClO₄
The electrolytic solution for Li ion cells according to claim 1 characterized by being chosen from the becoming group.

[Claim 6] The electrolytic solution for Li ion cells according to claim 1 characterized by the concentration of Li metal salt being 0.5-1.5M.

[Claim 7] The electrolytic solution for Li ion cells according to claim 1 characterized by said surface active agent being an urea system or a thiourea system surface active agent.

[Claim 8] The electrolytic solution for Li ion cells according to claim 1 characterized by being the nonionic surfactant chosen from the group which said surface active agent becomes from polyethylene-glycol wood ether and silicon poly para-phenylene oxide.

[Claim 9] The electrolytic solution for Li ion cells according to claim 1 with which the addition of said surfactant is characterized by being 0.05 - 3 % of the weight to the total amount of said mixed organic solvent and Li metal salt.

[Claim 10] Li ion cell containing the anode plate which consists of a Li multiple oxide, the cathode which consists of carbon material, Li metal salt dissolved in the mixed organic solvent and said solvent and a mixed organic solvent, and the electrolytic solution which contains 0.01 - 5% of the weight of a surfactant on the basis of Li metal salt total amount.

[Claim 11] Li ion cell according to claim 10 characterized by said carbon material being amorphous carbon material.

[Claim 12] Said mixed organic solvent is Li ion cell according to claim 10 characterized by including a high dielectric constant solvent and a hypoviscosity solvent.

[Claim 13] Li ion cell according to claim 12 characterized by being chosen from the group which said high dielectric constant solvent becomes from ethylene carbonate, propylene carbonate, and a gamma butyrolactone.

[Claim 14] Li ion cell according to claim 12 characterized by being chosen from the group which said hypoviscosity solvent becomes from dimethyl carbonate, diethyl carbonate, and dimethoxyethane.

[Claim 15] Said Li metal salt is LiPF₆, LiAsF₆, LiCF₃SO₃, LiN (CF₃ SO₂)₃, and LiBF₆. And LiClO₄ Li ion cell according to claim 10 characterized by being chosen from the becoming group.

[Claim 16] Li ion cell according to claim 10 characterized by the concentration of Li metal salt in the electrolytic solution being 0.5-1.5M.

[Claim 17] Li ion cell according to claim 10 characterized by said surface active agent being an urea system or a thiourea system surface active agent.

[Claim 18] Li ion cell according to claim 10 characterized by ***** which is the nonionic surfactant chosen from the group which said surface active agent becomes from polyethylene-glycol wood ether and silicon poly para-phenylene oxide.

[Claim 19] Li ion cell according to claim 10 by which the addition of said surfactant is characterized by being 0.05 - 3 % of the weight to the total amount of said mixed organic solvent and Li metal salt.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to Li ion cell which adopted the electrolytic solution for Li ion cells and it which start Li ion cell, especially are not easily decomposed by the reaction with a cathode active material.

[0002]

[Description of the Prior Art] While portable electronic devices, such as a camcorder, a laptop computer, and a cellular phone, are spread quickly recently, the improvement of the engine performance to a cell usable as these power sources is demanded. Li ion cell is capturing the spotlight as that which can **** in such a demand.

[0003] Li ion cell is a cell which was made filled up with the organic electrolytic solution with movable Li ion, or a polymer electrolyte between the anode plate which uses the matter in which the intercalation (intercalation) of Li ion and a day intercalation (deintercalation) are possible as an active material, cathode and an anode plate, and cathode, and was manufactured, and generates electrical energy by oxidation in case the intercalation / day intercalation of the Li ion are carried out in said anode plate and cathode, and the reduction reaction.

[0004] as the anode plate of said Li ion cell -- Li/Li⁺ electrode potential -- about 3 -4.5V -- although high potential is shown and the multiple oxide of the transition metals and Li in which the intercalation / day intercalation of Li ion are possible is mainly used -- as the example -- LiCoO₂, LiNiO₂, and LiMnO₂ etc. -- it is mentioned.

[0005] Moreover, structural as cathode and the carbon system matter with which the chemical potential at the time of the intercalation / day intercalation of Li metal which receives Li ion reversibly, maintaining an electrical property, or can be supplied, its alloy, or Li ion was mostly similar with Metal Li are mainly used. In this, although a carbon system cathode active material is classified into crystalline substance carbon material and amorphous carbon material according to the crystal structure, the hard carbon which was made to carbonize the soft carbon or giant-molecule resin which heat-treated the pitch at about 1000 degrees C, and obtained the graphite as amorphous carbon material as crystalline substance carbon material, and was obtained is mentioned.

[0006] Although the reversibility of a charge-and-discharge process is comparatively good, while crystalline substance carbon material has the demerit in which charge capacity is small, amorphous carbon material has demerit that nonreversible is large at the time of charge and discharge, although capacity is large compared with said crystalline substance carbon material. That is, in amorphous carbon material, while 70 - 80% of Li ion inserted in the carbon grid in the initial charge process is used in the following discharge process (irreversible capacity: 20 - 30%), in the case of crystalline substance carbon material, irreversible capacity is 10 - 15%.

[0007] It is known that irreversible capacity will change the magnitude according to the structure of reduction reaction extent of the structural property of the carbon material used as a cathode active material and the electrolytic solution and the solid electrolyte interface film (solid electrolyte interface

film:SEI film) formed in the front face of cathode.

[0008] That is, when the SEI film formed in the front face of a cathode active material is uneven and a lifting and the electrolytic solution are disassembled in an electrolytic-solution decomposition reaction by the electron in a cathode active material flowing out actively through said film, and making the electrolytic solution return, the irreversible capacity of a cathode active material is made increased by blocking the process in which the intercalation / day intercalation of the Li are carried out between carbon grids.

[0009] When irreversible capacity increases, it becomes impossible thus, to manufacture the cell in which it not only induces capacity reduction and life-shortening of a cell, but maximum capacity can be shown by the minimum weight.

[0010]

[Problem(s) to be Solved by the Invention] The technical technical problem which this invention tends to solve is by forming the uniform and precise SEI film in the front face of a cathode active material to offer the electrolytic solution for Li ion cells in which the decomposition reaction of the electrolytic solution is decreased and it deals.

[0011] Other technical technical problems which this invention tends to solve are by decreasing the decomposition reaction of the electrolytic solution by the carbon material cathode active material, and making the reversible capacitance of a cell increase to offer Li ion cell which made the life extend.

[0012]

[Means for Solving the Problem] That is, the technical technical problem of this invention is attained by following the (1) - (19).

[0013] (1) The electrolytic solution for Li ion cells which contains 0.01 - 5% of the weight of a surfactant on the basis of the total amount of Li metal salt dissolved in the mixed organic solvent and said solvent, and said mixed organic solvent and Li metal salt.

[0014] (2) Said mixed organic solvent is the electrolytic solution for Li ion cells given in the above (1) characterized by including a high dielectric constant solvent and a hypoviscosity solvent.

[0015] (3) The electrolytic solution for Li ion cells given in the above (2) characterized by being chosen from the group which said high dielectric constant solvent becomes from ethylene carbonate, propylene carbonate, and a gamma butyrolactone.

[0016] (4) The electrolytic solution for Li ion cells given in the above (2) characterized by being chosen from the group which said hypoviscosity solvent becomes from dimethyl carbonate, diethyl carbonate, and dimethoxyethane.

[0017] (5) Said Li metal salt is LiPF₆, LiAsF₆, LiCF₃SO₃, LiN(CF₃SO₂)₃, and LiBF₆. And LiClO₄. The electrolytic solution for Li ion cells given in the above (1) characterized by being chosen from the becoming group.

[0018] (6) The electrolytic solution for Li ion cells given in the above (1) whose concentration of Li metal salt is characterized by being 0.5-1.5M.

[0019] (7) The electrolytic solution for Li ion cells given in the above (1) said whose surface active agent is characterized by being an urea system or a thiourea system surface active agent.

[0020] (8) The electrolytic solution for Li ion cells given in the above (1) characterized by being the nonionic surfactant chosen from the group which said surface active agent becomes from polyethylene-glycol wood ether and silicon poly para-phenylene oxide.

[0021] (9) The electrolytic solution for Li ion cells given in the above (1) whose addition of said surfactant is characterized by being 0.05 - 3 % of the weight to the total amount of said mixed organic solvent and Li metal salt.

[0022] (10) Li ion cell containing the anode plate which consists of a Li multiple oxide, the cathode which consists of carbon material, Li metal salt dissolved in the mixed organic solvent and said solvent and a mixed organic solvent, and the electrolytic solution which contains 0.01 - 5% of the weight of a surfactant on the basis of Li metal salt total amount.

[0023] (11) Li ion cell given in the above (10) said whose carbon material is characterized by being amorphous carbon material.

[0024] (12) Said mixed organic solvent is Li ion cell given in the above (10) characterized by including a high dielectric constant solvent and a hypoviscosity solvent.

[0025] (13) Li ion cell given in the above (12) characterized by being chosen from the group which said high dielectric constant solvent becomes from ethylene carbonate, propylene carbonate, and a gamma butyrolactone.

[0026] (14) Li ion cell given in the above (12) characterized by being chosen from the group which said hypoviscosity solvent becomes from dimethyl carbonate, diethyl carbonate, and dimethoxyethane.

[0027] (15) said Li metal salt -- LiPF_6 , LiAsF_6 , and LiCF_3SO_3 , $\text{LiN}(\text{CF}_3\text{SO}_2)_3$, and LiBF_6 And LiClO_4 Li ion cell given in the above (10) characterized by being chosen from the becoming group.

[0028] (16) Li ion cell given in the above (10) whose concentration of Li metal salt in the electrolytic solution is characterized by being 0.5-1.5M.

[0029] (17) Li ion cell given in the above (10) said whose surface active agent is characterized by being an urea system or a thiourea system surface active agent.

[0030] (18) Li ion cell given in the above (10) characterized by ***** which is the nonionic surfactant chosen from the group which said surface active agent becomes from polyethylene-glycol wood ether and silicon poly para-phenylene oxide.

[0031] (19) Li ion cell given in the above (10) whose addition of said surfactant is characterized by being 0.05 - 3 % of the weight to the total amount of said mixed organic solvent and Li metal salt.

[0032]

[Embodiment of the Invention] The technical technical problem of this invention is made with the electrolytic solution for Li ion cells containing the surfactant of 0.01 - 5 % of the weight of total amount contrast of Li metal salt dissolved in the mixed organic solvent and said solvent, and said mixed organic solvent and Li metal salt.

[0033] Moreover, other technical technical problems of this invention are made by Li ion cell containing the electrolytic solution containing the surfactant of 0.01 - 5 % of the weight of total amount contrast of Li metal salt dissolved in the anode plate which consists of a Li multiple oxide, the cathode which consists of carbon material, and a mixed organic solvent and said solvent, and said mixed organic solvent and Li metal salt.

[0034] In the electrolytic solution for Li ion cells by this invention, it is desirable to use a nonionic surfactant like an urea system, a thiourea system surface active agent, polyethylene-glycol wood ether, or silicon poly para-phenylene oxide (SiPPO) as said surface active agent.

[0035] The addition of such a surfactant is 0.05 - 3 % of the weight desirably 0.01 to 5% of the weight to the total amount of a mixed organic solvent and Li metal salt, as mentioned above. If the addition of a surfactant is less than 0.01 % of the weight, the addition effectiveness is minute, and while the SEI film formed on a cathode active material is uneven as usual, in exceeding 5 % of the weight, there is a trouble of reducing ion conductivity, by forming the SEI film thickly too much.

[0036] Moreover, although it is desirable to maintain high electrical conductivity by using the mixed solvent which contains a high dielectric constant solvent and a hypoviscosity solvent as said mixed organic solvent, as said high dielectric constant solvent, ethylene carbonate, propylene carbonate, a gamma butyrolactone, etc. are mentioned, and dimethyl carbonate, diethyl carbonate, dimethoxyethane, etc. are mentioned as a hypoviscosity solvent.

[0037] As said Li metal salt which can dissolve in such a mixed organic solvent, they are LiPF_6 , LiAsF_6 , LiCF_3SO_3 , $\text{LiN}(\text{CF}_3\text{SO}_2)_3$, and LiBF_6 . And LiClO_4 It can be used choosing. Moreover, as for the concentration of Li metal salt in the electrolytic solution, it is desirable that it is 0.5-1.5M.

[0038] On the other hand, in Li ion cell by this invention, when using amorphous carbon material as said cathode active material, desirable effectiveness is acquired especially. The soft carbon which heat-treats precursors, such as a pitch, at the temperature of about 1000 degrees C as such amorphous carbon material, and is obtained, and the hard carbon which is made to carbonize giant-molecule resin and is obtained can be used. Here, as a precursor of said soft carbon, the crude oil (petroleum oil) of a petroleum pitch, a coal tar pitch, or low molecular weight etc. is used, and polyimide resin, furan resin, phenol resin, polyvinyl alcohol resin, cellulosic resin, an epoxy resin, or macromolecule resin like

polystyrene resin is used as said hard carbon precursor.

[0039] The principle of this invention is improving the property of the solid electrolyte interface film (henceforth, SEI film) in which it is generated by side reaction at the time of charge, and deals by adding a surfactant to the electrolytic solution. That is, the flow of the electron which flows out of a cathode active material is fully uniform possible [prevention], and precise, decrease reduction of the electrolytic solution by form the SEI film which has high ionic conductivity to Li ion, by receive Li ion reversibly or emit it through said film, whenever [of a cell / reversible] is make to increase and, thereby, the cycle property and life of a cell can be prolong.

[0040]

[Example] Although an example and the example of a comparison are given and this invention is explained in more detail hereafter, this invention is not limited to this.

[0041] LiMn 2O4 of an example 1 anode-plate active material After carrying out the maximum removal of the moisture which was dried at 130 degrees C under the vacuum ambient atmosphere for 12 hours, and was contained in the active material, this was mixed with the polytetrafluoroethylene dissolved in acetylene black and N-methyl pyrrolidone solution, and the anode plate active material was manufactured. After casting this anode plate active material for aluminium foil by the thickness of 150 micrometers, it was made to dry for 5 hours, it stuck by pressure and fabricated in oven after that, and the anode plate was manufactured.

[0042] Subsequently, after carrying out crosslinking reaction of the coal tar from which the impurity was removed and compounding a precursor, it manufactured to the powder which heat-treats this at about 1000 degrees C, and is used as a cathode active material. Cathode was manufactured using this powder.

[0043] Then, it is LiPF6 as the electrolytic solution to the mixed solvent of the ethylene carbonate of a 2:1 ** ratio (volume ratio), and dimethyl carbonate. The nonaqueous organic electrolytic solution which added 0.5g thiourea in 100g of solutions dissolved in 1 M concentration was manufactured.

[0044] Using the anode plate, the cathode, and the electrolytic solution which were manufactured as mentioned above, an assembly, its initial charge capacity, initial discharge capacity, cell effectiveness, and the discharge capacity after 50 cycles were measured, and Li ion cell was shown in Table 1.

[0045] If it removed manufacturing the electrolytic solution, using the addition of example 2 thiourea as 1g, after manufacturing an anode plate, cathode, and an electrolyte like an example 1 and assembling Li ion cell using this, the initial charge capacity, initial discharge capacity, cell effectiveness, and the discharge capacity after 50 cycles were measured, and it was shown in Table 1.

[0046] If it removed adding 0.3g polyethylene-glycol wood ether instead of example 3 thiourea, and manufacturing the electrolytic solution, after assembling Li ion cell by the same approach as an example 1, the initial charge capacity, initial discharge capacity, cell effectiveness, and the discharge capacity after 50 cycles were measured, and it was shown in Table 1.

[0047] At the time of the example electrolytic-solution manufacture of a comparison, if it removed not adding thiourea, Li ion cell was manufactured by the same approach as an example 1, the initial charge capacity, initial discharge capacity, cell effectiveness, and the discharge capacity after 50 cycles were measured, and it expressed to Table 1.

[0048]

[Table 1]

	実施例 1	実施例 2	実施例 3	比較例
初期充電容量(mAh/g)	432	441	435	437
初期放電容量(mAh/g)	316	340	361	306
電池効率(%)	73	77	83	70
50 サイクル後の放電容量 (mAh/g)	278.1	906	337	244.8

[0049] From said result, compared with Li ion cell (example of a comparison) which uses the usual electrolytic solution with which a surfactant is not added in the case of Li ion cell (examples 1, 2, and 3) of this invention which uses the electrolytic solution with which the surfactant of the specified quantity

was added, since the discharge capacity after 50 cycles is also large, it makes the life of a cell improve and cell effectiveness is not only excellent, but gets.

[0050]

[Effect of the Invention] According to the Li ion cell of this invention, by controlling side reaction like disassembly of the electrolytic solution using the electrolytic solution with which the surfactant was added, the trouble of a high irreversible capacity which is the fault of Li ion cell which adopted the cathode which consists of carbon material, especially amorphous carbon material is improved, and, thereby, the charge-and-discharge property and life of a cell are improved.

[Translation done.]